

Rapid Reaction of Sulfide with Hydrogen Peroxide and Formation of Different Final Products by Freezing Compared to Those in Solution

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ABSTRACT: The reaction of sulfide with hydrogen peroxide in an aqueous solution at pH 9 produces thiosulfate, sulfite, and an unknown sulfur compound as intermediates, and, finally, all sulfides convert to sulfate (Chen and Gupta, *Environ Lett* 1973, 4, 187–200; Yokosuka et al., *Nihon Kagaku Kaishi* 1975, 11, 1901–1909; Hoffmann, *Environ Sci Technol* 1977, 11, 61–66; Ràbai et al., *J Phys Chem* 1992, 96, 5414–5419). This reaction was found to be accelerated by freezing. The decomposition rate of sulfide by H₂O₂ in freezing at –15°C was about 5 times faster than the maximum decomposition rate in solution at 25°C. The decomposition of sulfide by freezing obeys zero-order kinetics, and the rate coefficient was 11.9 mol dm^{–3} min^{–1} at a freezing rate of 0.83 cm³ min^{–1}. Zero-order kinetics is one of the characteristics of freezing rate-controlled reactions. Thiosulfate, sulfite, and an unknown sulfur compound were also observed as intermediates in the reaction by freezing. The decomposition of thiosulfate obeys first-order kinetics, and the rate coefficient was 0.0496 min^{–1} at –15°C. The rate coefficient in freezing at –15°C is about 47 times faster than that in solution at 25°C. Sulfide, thiosulfate, and sulfite were consumed after 90 min. However, the unknown sulfur compound was not oxidized and was preserved in ice for a long time even in the presence of an excess of hydrogen peroxide. The concentration of an unknown sulfur compound in the frozen sample can be changed by changing the concentration of H₂O₂ and the pH of the solution. Freezing could be used for rapid preparation and preservation of unstable substances in solution. © 2003 Wiley Periodicals, Inc. *Int J Chem Kinet* 35: 198–205, 2003

INTRODUCTION

Some reactions have been known to be accelerated by freezing or in frozen systems compared to those

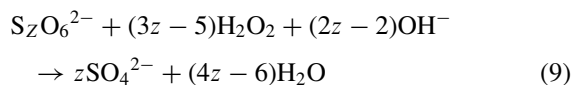
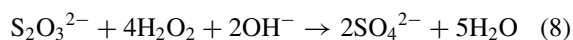
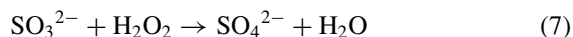
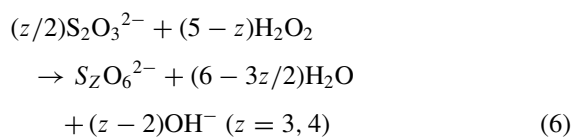
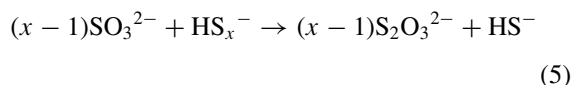
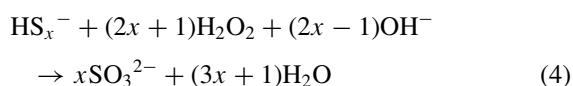
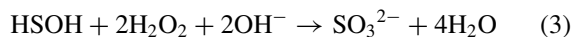
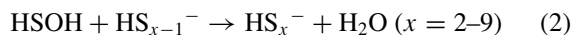
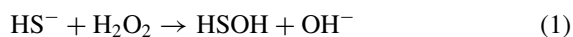
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in solution [1–10]. In the 1960s, acceleration of reactions by freezing or in frozen systems had been investigated mainly in food chemical, biochemical, and organic fields. After 1985, more simple reactions have also been reported to be accelerated by freezing. The reactions of nitrite with dissolved oxygen [9–11], sulfite with oxygen [9], ferricyanate with potassium cyanide [8], ascorbic acid with oxygen [12], potassium iodide with oxygen under acidic condition [13], and so on are accelerated by freezing. Despite such many reports, the mechanism of acceleration of reactions by freezing or in frozen systems has not been understood completely yet.

A systematic review of the acceleration mechanism has been summarized by O. Fennema [7]: (1) freeze-concentration, (2) catalytic effect of ice, (3) hydrolysis due to change of pH, (4) desirable orientation of reactants in ice, and (5) difference in dielectric constants between water and ice. Among these mechanisms, it is most likely that freeze-concentration into an unfrozen solution in ice is a main cause of acceleration. Pincock also reviewed the reactions in frozen systems [6]. He concluded that freeze-concentration was the only cause of acceleration in frozen systems. The effects of freeze-concentration are different in different types of ions. The difference in the concentration effects on a cation and an anion causes an electrical potential generation between ice and solution. For example, +214 V of a potential of an ice phase with respect to a liquid phase is generated by freezing a 15 $\mu\text{mol dm}^{-3}$ $(\text{NH}_4)_2\text{CO}_3$ aqueous solution, and –90 V is generated by freezing a 25 $\mu\text{mol dm}^{-3}$ KCN aqueous solution [14]. Electrochemical reactions due to the potential thus formed may be possible, but no product formed by an electrochemical reaction could be detected by common analytical methods because the amounts of products are very small. The amounts of products are very small because the electric current is produced by the difference between ice and solution in the separation of cations and anions and the potential is generated exclusively under conditions of low reactant concentrations. The potential generated is neutralized by transferring the protons between solution and ice, which causes changes in the pHs of the solution and the ice. The change in the pH of the solution causes hydrolysis.

Freezing is a common method of preserving chemicals and food. Reactants cannot move easily in solid, and therefore, reactions are suppressed. Lower temperature in solid state than that in liquid state is also the cause of suppression for reactions. As a result, reactions are terminated when solution is frozen. If reactions that are accelerated by freezing do not proceed completely until the whole sample is frozen and produce intermediates, those can be stored in ice.

The reaction of sulfide with H_2O_2 in an aqueous solution has already been reported [15–17]. Sulfide ion reacts with H_2O_2 to form HSOH [Eq. (1)]. The formed HSOH reacts with HS^- to form polysulfide [HS_x^- , $x = 2$ –9; Eq. (2)]. In this case, the following reactions proceed. Reactions of HSOH or HS_x^- with H_2O_2 form sulfite [Eqs. (3) and (4)]. The formed sulfite reacts with HS_x^- to form thiosulfate [Eq. (5)]. Thiosulfate reacts with H_2O_2 to form polythionate [Eq. (6)]. Finally, sulfite, thiosulfate, and polythionate react with H_2O_2 to form sulfate [Eqs. (7)–(9)]. The reactions are fast under neutral or alkaline conditions but very slow under acidic conditions. Therefore, under alkaline conditions, all sulfur contents are oxidized to sulfate by excess amounts of H_2O_2 . This report shows that the reaction of sulfide with H_2O_2 is accelerated by freezing and that polythionate, as an intermediate of the reaction, is not completely oxidized to sulfate under alkaline conditions even under excess amounts of H_2O_2 .



EXPERIMENTAL

All reagents, obtained from Wako Pure Chemicals, Inc., were reagent grade and used without further purification. Pure water was prepared by Milli-Q Labo using distilled water. The resistivity of the pure water was higher than 18.2 $\text{M}\Omega \text{ cm}$. Sodium sulfide was dissolved and adjusted to the desired concentration with pure water, which was bubbled with N_2 gas for more than 20 min to eliminate dissolved oxygen. An aliquot of an oxygen-free sulfide solution (10 cm^3) was put into

a polypropylene syringe (i.d. 1.58 cm) sealed with a septum [10]. Using a microsyringe, a hydrogen peroxide solution of trace volume was added through the septum to the sulfide solution in the sealed syringe to start the reaction at room temperature. This point of time was defined as the initial time. The concentration of sodium sulfide was adjusted at about $100 \mu\text{mol dm}^{-3}$. The concentration of sulfide was sometimes slightly different from $100 \mu\text{mol dm}^{-3}$, and the concentration was corrected as described below. The typical concentration of H_2O_2 was about $600 \mu\text{mol dm}^{-3}$ for the freezing experiments. The polypropylene syringe containing the mixed solution was immediately transferred to a thermostat at -15°C for the freezing experiments or 25°C for the control experiments. Details of the freezing and thawing methods are described in previous studies [9,10]. Even when the sample was treated in this way, however, small productions of sulfite, thiosulfate, and sulfate could not be prevented. The pH of the solution, which was not adjusted, was about 9 for approximately $100 \mu\text{mol dm}^{-3}$ of the sulfide solution. When the pH was adjusted to pH 10, a NaOH aqueous solution was used. The ionic strength was uncontrolled in all experiments because additional salts change reactions by freezing [10]. The time profiles of each ion concentration were obtained by a set of different runs in the freezing experiments. The reproducibility can be confirmed by the time profile.

The $\text{p}K_{\text{a}1}$ and $\text{p}K_{\text{a}2}$ of H_2S were 7.05 and 12 [18], respectively, and the sodium sulfide solution was alkaline. The $\text{p}K_{\text{a}1}$ and $\text{p}K_{\text{a}2}$ of H_2SO_3 were 1.85 and 7.2 [18], respectively, and those of $\text{H}_2\text{S}_2\text{O}_3$ were 0.6 and 1.6 [19], respectively. The species in the present experiments were HS^- , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, and SO_4^{2-} .

The concentrations of sulfur compounds in the frozen sample were analyzed after the sample was completely thawed in a hot-water bath within a few minutes [10]. Anions other than polythionates were analyzed with IC-7000 or IC-100 Ionchromatographic Analyzers from the Yokogawa Co., Ltd. An ICS-23 column with an eluent of an 8 mM Na_2CO_3 solution was used to analyze thiosulfate and sulfate, and an ICS-44 column with an eluent of a 4 mM Na_2CO_3 and 4 mM NaHCO_3 mixture was used to analyze sulfite and sulfate. Sulfide was determined by the methylene-blue method [20]. The concentration of sulfide was sometimes confirmed by ion chromatography after all sulfur content was oxidized to sulfate. Trithionate and tetrathionate were confirmed with a GL Science, Inc., PU 610 HPLC-UV detector (218 nm) [21]. The column was a GL Science, Inc., Inertsil ODS-3, and the eluent solution was a 3 mM $(\text{C}_4\text{H}_9)_4\text{NOH}$ and 2 mM Na_2CO_3 mixture in $(26 + 74) \text{CH}_3\text{CN} + \text{H}_2\text{O}$.

RESULTS AND DISCUSSION

Reaction of Sulfide with Hydrogen Peroxide in an Aqueous Solution at Room Temperature

A reaction of sulfide ion with hydrogen peroxide in an aqueous solution produces sulfite and thiosulfate ions and finally sulfate [15,16,22,23]. The reaction rate in the aqueous solution is not very fast. Figure 1 shows the time profile of the reaction in the aqueous solution at 25°C and an initial pH of 9. Almost all sulfide ions were consumed in 210 min. Sulfite and thiosulfate were produced first, and then sulfate was gradually formed. These results were consistent with the literature [23]. All of the sulfur was changed to sulfate within 24 h, and no other sulfur compounds were detected. In the course of the reaction, unknown intermediates, which are the difference between the initial S concentration and the total S detected, were observed. We had checked for the possibility that various sulfur compounds, such as polysulfide, sulfur, $\text{S}_2\text{O}_x^{2-}$ ($x = 4-8$), and $\text{S}_y\text{O}_6^{2-}$ ($y = 3, 4$), would be the unknown sulfur compounds. We found that one of the unknown intermediates was a tetrathionate ion. Tetrathionate was confirmed by an HPLC-UV detector as mentioned in the experimental section. This result is consistent with the results by Yokosuka et al. [23].

The decomposition rate of sulfide by H_2O_2 is reported to obey Eq. (10) [17].

$$d[\text{H}_2\text{S}]_{\text{T}}/dt = -k[\text{H}_2\text{S}]_{\text{T}}[\text{H}_2\text{O}_2] \quad (10)$$

Here, $[\text{H}_2\text{S}]_{\text{T}}$ denotes total sulfide. The reported k value [17] is

$$\log k = 12.04 - 2641/T - 0.186 \times \text{pH} \quad (11)$$

The decomposition of sulfide showed a first-order decay (Fig. 1), and it is presumed that the concentration of H_2O_2 was almost constant until most of the sulfide was decomposed. The least-squares fitting of the line $\ln[\text{total sulfide}]$ versus time showed a good straight line with a slope of -0.0360 and a squared correlation coefficient, r^2 , of 0.995. The first-order rate constant from Eq. (11) of 0.0383 min^{-1} calculated at $1200 \mu\text{mol dm}^{-3}$ of H_2O_2 at 25°C and pH 9 agreed with the obtained value of 0.0360 min^{-1} . The decomposition of thiosulfate by H_2O_2 also obeyed first-order kinetics for thiosulfate, which is also consistent with the literature [23]. The first-order rate constant for the decomposition of thiosulfate was $1.15 \times 10^{-3} \text{ min}^{-1}$.

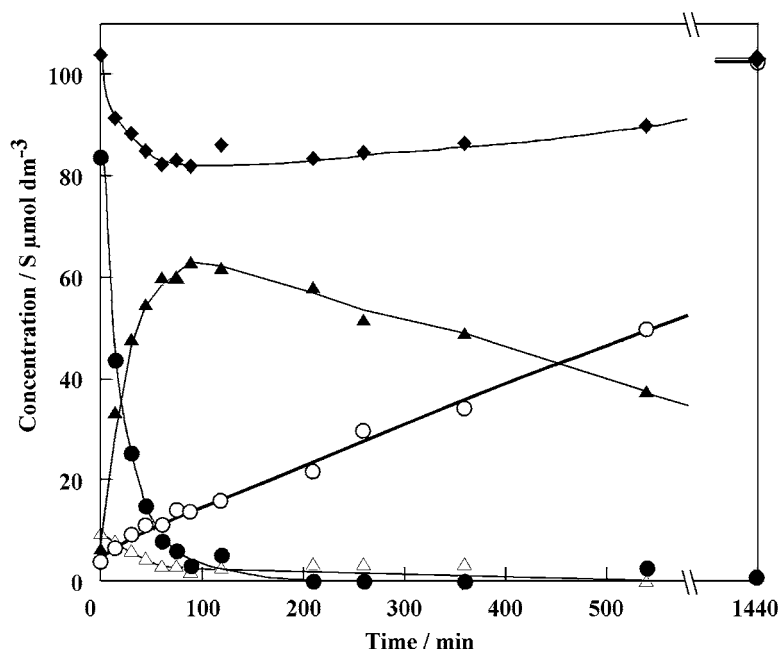


Figure 1 Time profile of the reaction of sulfide ion with hydrogen peroxide in solution at 25°C and pH 9. The initial concentrations of sulfide ion and hydrogen peroxide were 100 and 1200 $\mu\text{mol dm}^{-3}$, respectively. \bullet , S^{2-} ; \blacktriangle , $\text{S}_2\text{O}_3^{2-}$; \triangle , SO_3^{2-} ; \circ , SO_4^{2-} ; \blacklozenge , total S detected. The difference between initial S^{2-} concentration and total S concentration corresponds to tetrathionate concentration (see text).

Reaction of Sulfide with Hydrogen Peroxide by Freezing

Figure 2 shows the results by freezing under the above conditions with the exceptions of the reaction temperature of -15°C and the concentration of H_2O_2 . The reaction showed an induction period (a few minutes) corresponding to the beginning of freezing, and, after that, the reaction proceeded according to a zero-order reaction until the end of freezing (12 min). The end of freezing is defined by visual observation, that is, the time at which the center of the sample changes to an opaque dendrite-like view consisting of small bubbles. The slope of the least-squares fitting line from 5 to 12 min (4 points) is -11.9 , and the squared correlation coefficient, r^2 , is 0.994. The apparent zero-order rate constant is $11.9 \text{ mol dm}^{-3} \text{ min}^{-1}$. The zero-order reaction, which is also reported in the reaction of nitrous acid with dissolved oxygen, is one of the characteristics of freezing rate-controlled reactions. Despite the lower concentration of H_2O_2 in the case of the freezing experiment ($600 \mu\text{mol dm}^{-3}$ in the freezing experiment and $1200 \mu\text{mol dm}^{-3}$ in the solution experiment) and the lower temperature (-15°C), the reaction was much faster than that in the solution at 25°C . The decomposition rate of sulfide by H_2O_2 in freezing at -15°C was about 5 times faster than the maximum rate in solution at 25°C . Most of the sulfides were consumed within

12 min in the freezing experiment and within 210 min in the solution. This could be due to freeze-concentration. The intermediates, sulfite and thiosulfate, were also produced in the freezing experiment. The thiosulfate concentration reached its maximum when the sample was completely frozen, and then decreased. The rate of decrease of thiosulfate in ice was much faster than it was in the solution. The decay curve of thiosulfate is observed to be a first-order decay. The natural logarithm of the concentration of thiosulfate versus time showed a straight line with a slope of -0.0496 and a squared correlation coefficient of 0.992 from 12 to 90 min. The first-order decay rate constant of thiosulfate is 0.0496 min^{-1} . The reaction rate of thiosulfate decomposition by H_2O_2 in frozen solution at -15°C is about 43 times faster than that in solution at 25°C . The oxidation reaction of sulfide with H_2O_2 occurs only during freezing, and the reaction temperature could be slightly under 0°C . The oxidation reaction of thiosulfate with H_2O_2 occurred after the entire sample was frozen. The eutectic point of thiosulfate is -11°C , and, therefore, it seems that the unfrozen solution cannot exist in ice. However, the reaction did proceed. This means that the eutectic point is measured only in a pure system, but, in the freezing reaction, there are several species in the system, making it a multicomponent system. In this case, the eutectic point for a single salt cannot be used for the estimation of the existence of

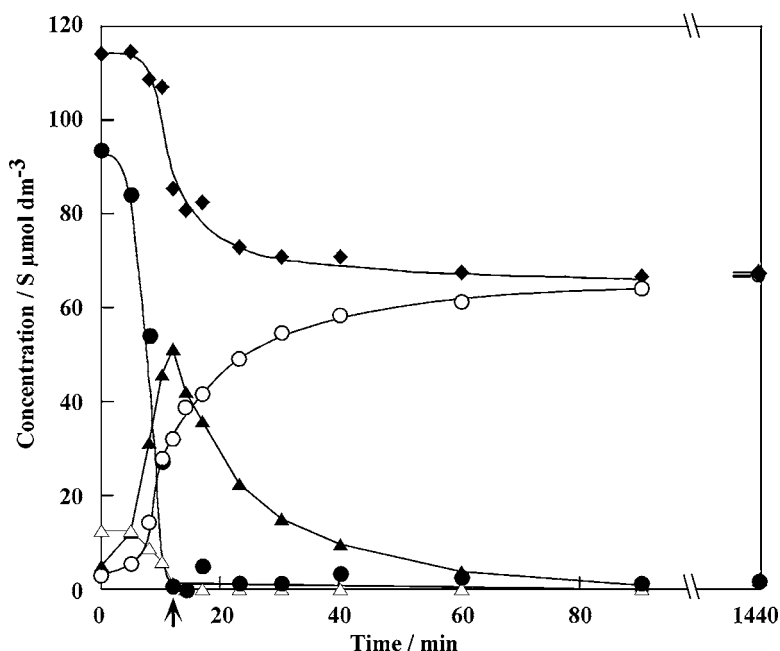


Figure 2 Time profile of the reaction of sulfide ion with hydrogen peroxide by freezing at -15°C and pH 9. The initial concentrations of sulfide ion and hydrogen peroxide were 100 and $600\ \mu\text{mol dm}^{-3}$, respectively. ●, S^{2-} ; ▲, $\text{S}_2\text{O}_3^{2-}$; △, SO_3^{2-} ; ○, SO_4^{2-} ; ◆, total S detected. The difference between initial S^{2-} concentration and total S concentration corresponds to tetrathionate concentration (see text). The arrow shows the time when the whole sample was frozen (see text).

the unfrozen solution. The eutectic point in the present system must be below -15°C . Thus, the reaction of sulfide with H_2O_2 by freezing is a very interesting system because the accelerations of the reactions can be observed both in the course of freezing and after being frozen.

An unknown sulfur compound was also observed in the freezing experiment in Fig. 2. Furthermore, not all of the sulfurs were converted to sulfate even after being frozen for 24 h. In order to clarify that this is not due to lower concentration of H_2O_2 , the time profiles of sulfur contents were investigated at various concentrations of H_2O_2 .

Effect of Concentration of H_2O_2 on the Reaction by Freezing

Figure 3 shows time profiles of the reaction by freezing at 0, 180, and $300\ \mu\text{mol dm}^{-3}$ of H_2O_2 and $100\ \mu\text{mol dm}^{-3}$ of sulfide. At $0\ \mu\text{mol dm}^{-3}$ of H_2O_2 , most of the sulfide was not oxidized. Small amounts of sulfur oxides were produced probably due to reactions with trace amounts of dissolved oxygen. At $180\ \mu\text{mol dm}^{-3}$ of H_2O_2 , not all of the sulfide was oxidized, and most of the H_2O_2 was consumed to form thiosulfate. Small amounts of an unknown sulfur compound were also observed. Because of insufficient amounts of H_2O_2 compared to amounts of

sulfide, formed thiosulfate was not decomposed. At $300\ \mu\text{mol dm}^{-3}$ of H_2O_2 , all of the sulfide was decomposed, and thiosulfate concentration had a maximum value similar to Fig. 2. However, not all of the sulfide was oxidized by H_2O_2 . The concentrations of the unknown sulfur compound, which corresponded to the difference between initial sulfide and total S concentrations, were changed by initial H_2O_2 concentration. In all cases in the present experiments, changes in concentrations of sulfur contents were not observed after 40 min. Figure 4 shows the final products of the reaction of sulfide with various concentrations of H_2O_2 . The freezing time was 4 h in all cases. Up to $250\ \mu\text{mol dm}^{-3}$ of H_2O_2 , sulfide, sulfite, thiosulfate, sulfate, and the unknown sulfur compound were detected. Up to $600\ \mu\text{mol dm}^{-3}$ of H_2O_2 , thiosulfate, sulfate, and the unknown sulfur compound remained in the thawed sample. Over $600\ \mu\text{mol dm}^{-3}$ of H_2O_2 , only sulfate, and the unknown sulfur compound were observed. Even at $1200\ \mu\text{mol dm}^{-3}$ of H_2O_2 (the same concentration as in Fig. 1), unknown sulfur compound still remained. The unknown sulfur compound was stable in ice for at least several days. It is reported that H_2O_2 is decomposed by freezing in the presence of trace amounts of metal ions [4]. However, enough amounts of H_2O_2 was detected in the thawed sample. It is concluded that the unknown sulfur compound can be stored in ice for a long time.

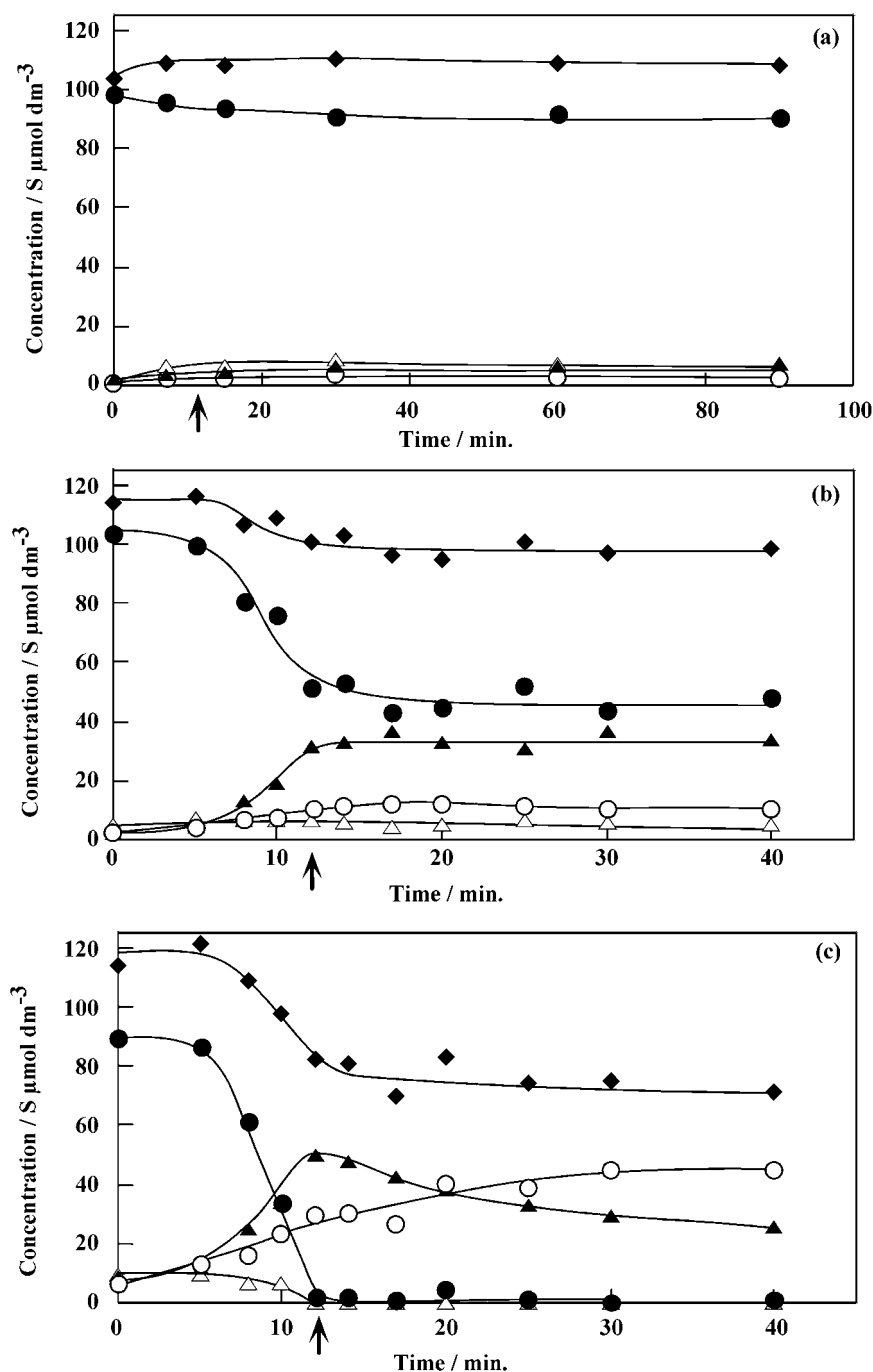


Figure 3 Time profile of the reaction by freezing at 0, 180, and 300 $\mu\text{mol dm}^{-3}$ of H_2O_2 and 100 $\mu\text{mol dm}^{-3}$ of sulfide. The initial concentration of sulfide was 100 $\mu\text{mol dm}^{-3}$ and that of H_2O_2 was (a) 0 $\mu\text{mol dm}^{-3}$, (b) 180 $\mu\text{mol dm}^{-3}$, (c) 300 $\mu\text{mol dm}^{-3}$. ●, S^{2-} ; ▲, $\text{S}_2\text{O}_3^{2-}$; △, SO_3^{2-} ; ○, SO_4^{2-} ; ♦, total S detected. The arrows show the time when the whole sample was frozen.

Identification of Unknown Sulfur Compound in the Reaction by Freezing

With low temperature and a high concentration of thiosulfate, trithionate is reported to be produced in

the reaction of thiosulfate with H_2O_2 [24]. It is most likely that the unknown sulfur compound is trithionate under the above freezing conditions due to freeze-concentration. However, we detected tetrathionate but not trithionate by HPLC as described above. Under the

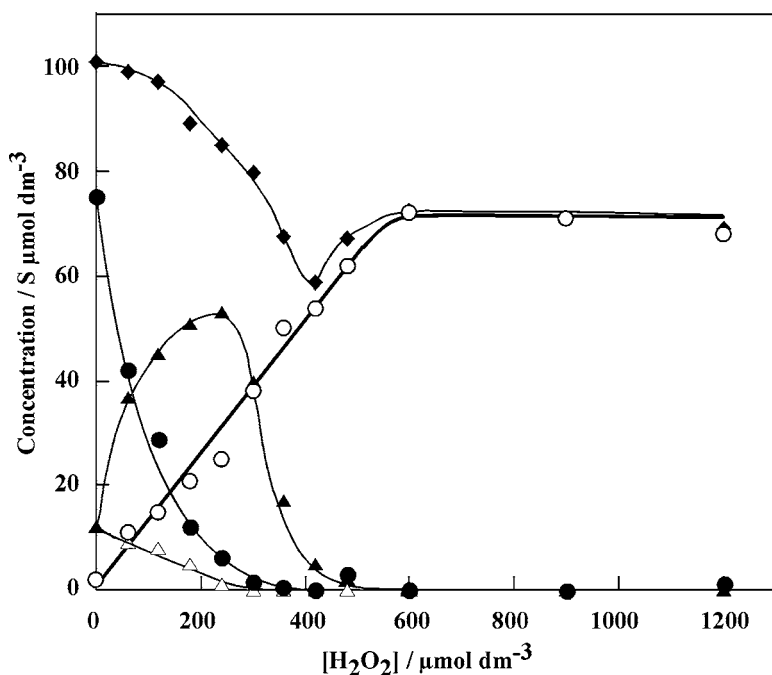


Figure 4 Final products (after 4 h) of the reaction of sulfide ion with various concentrations of hydrogen peroxide by freezing at -15°C and pH 9. The initial concentration of sulfide ion was $100\ \mu\text{mol dm}^{-3}$. \bullet , S^{2-} ; \blacktriangle , $\text{S}_2\text{O}_3^{2-}$; \triangle , SO_3^{2-} ; \circ , SO_4^{2-} ; \blacklozenge , total S detected. The difference between initial S^{2-} concentration and total S concentration corresponds to tetrathionate concentration (see text).

conditions for freezing given above, it is considered that the concentration of thiosulfate in the course of freezing did not reach to a sufficient concentration for the formation of trithionate.

The Reaction by Freezing at pH 10

Figure 5 shows a time profile of the reaction by freezing at pH 10. The results were similar to Fig. 2. However,

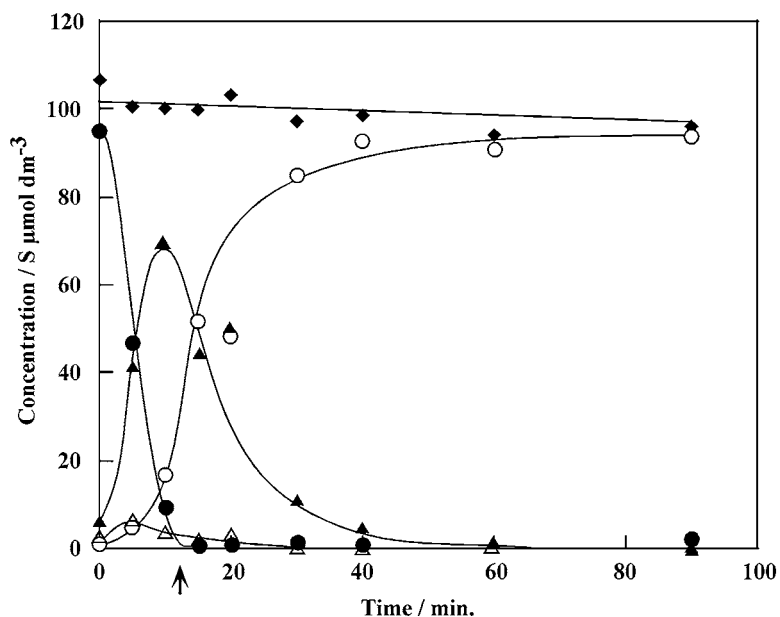


Figure 5 Time profile of the reaction of sulfide ion with hydrogen peroxide by freezing at -15°C and pH 10. The initial concentrations of sulfide ion and hydrogen peroxide were 100 and $600\ \mu\text{mol dm}^{-3}$, respectively. \bullet , S^{2-} ; \blacktriangle , $\text{S}_2\text{O}_3^{2-}$; \triangle , SO_3^{2-} ; \circ , SO_4^{2-} ; \blacklozenge , total S detected. The arrow shows the time when the whole sample was frozen.

the unknown sulfur content was not observed, and all sulfides were oxidized to sulfate. This result suggests that the formation and concentration of tetrathionate can be controlled by changing pH of the solution. From the above results, it is expected that concentration and composition of frozen sample can be controlled by adjusting pH and concentration of hydrogen peroxide.

There are two possibilities that tetrathionate is not oxidized to sulfate in the freezing experiment at pH 9: (1) activation energy of the reaction of tetrathionate with H_2O_2 is very large, but that of the production reaction of tetrathionate is not so large; and therefore, a decrease of the reaction rate of tetrathionate with H_2O_2 because of lower temperature in the freezing experiment is greater than the acceleration due to the concentration-effect by freezing; (2) the reaction pathway is altered. For example, it is known that pH is changed during freezing [7,10], and pH in the freezing experiment is low as the oxidation of tetrathionate does not occur. Therefore, at lower pH in the freezing experiment, formed tetrathionate remained in the frozen sample.

The use of freezing can be a faster preparation method for tetrathionate and that the preparation method itself can be the preservation method for tetrathionate under the appropriate experimental condition.

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